

CLAIMS

1. A method for the formation of a metal film which comprises the steps of feeding a raw material gas containing a halogen into an inlet vessel having a perforated plate made of metal; converting the raw material gas into a plasma to generate a raw material gas plasma; etching the perforated plate with the raw material gas plasma to produce a precursor composed of the metallic component contained in the perforated plate and the halogen contained in the raw material gas; converting a reducing gas into a plasma to generate a reducing gas plasma; after discharging the precursor from the inlet vessel, passing the precursor through a rotating magnetic field so as to cause the precursor to travel toward a substrate in an accelerated manner; and passing the precursor through the reducing gas plasma to remove the halogen from the precursor and directing the resulting metallic ion or neutral metal onto the substrate to form a thin metal film on the substrate.

2. A method for the formation of a metal film which comprises the steps of feeding a raw material gas containing a halogen into an inlet vessel having a perforated plate made of metal; converting the raw material gas into a plasma to generate a raw material gas plasma; etching the perforated plate with the raw material gas plasma to produce a precursor composed of the metallic component contained in the perforated plate and the halogen contained in the raw material gas;

passing a high-frequency electric current through an electrode having openings that allow the precursor to flow therethrough, and thereby converting a reducing gas into a plasma to generate a reducing gas plasma; and passing the precursor
5 through the reducing gas plasma to remove the halogen from the precursor and directing the resulting metallic ion or neutral metal onto the substrate to form a thin metal film on the substrate.

3. A method for the formation of a metal film which
10 comprises the steps of feeding a raw material gas containing a halogen into an inlet vessel having a perforated plate made of metal; converting the raw material gas into a plasma to generate a raw material gas plasma; etching the perforated plate with the raw material gas plasma to produce a precursor
15 composed of the metallic component contained in the perforated plate and the halogen contained in the raw material gas; producing an atomic reducing gas between the perforated plate and a substrate by heating a reducing gas to a high temperature; and, after discharging the precursor from the
20 inlet vessel, passing the precursor through the atomic reducing gas to remove the halogen from the precursor and directing the resulting metallic ion or neutral metal onto the substrate to form a thin metal film on the substrate.

4. A method for the formation of a metal film which
25 comprises the steps of bringing a raw material gas containing a halogen into contact with a hot metallic filament and

thereby etching the filament with the raw material gas to produce a precursor composed of the metallic component contained in the filament and the halogen contained in the raw material gas; producing an atomic reducing gas by heating a reducing gas to a high temperature; and passing the precursor through the atomic reducing gas to remove the halogen from the precursor and directing the resulting metallic ion or neutral metal onto a substrate to form a thin metal film on the substrate.

5 5. A method for the formation of a metal film which comprises the steps of bringing a raw material gas containing a halogen into contact with a hot metallic filament and thereby etching the filament with the raw material gas to produce a precursor composed of the metallic component contained in the filament and the halogen contained in the raw material gas; passing a high-frequency electric current through an electrode having openings that allow the precursor to flow therethrough, and thereby converting a reducing gas into a plasma to generate a reducing gas plasma; and passing the precursor through the reducing gas plasma to remove the halogen from the precursor and directing the resulting metallic ion or neutral metal onto a substrate to form a thin metal film on the substrate.

25 6. A method for forming a metal film as claimed in any of claims 1 to 5 wherein the perforated plate or filament contains copper and the precursor is Cu_xCl_y .

7. A method for forming a metal film as claimed in any of claims 1 to 6 wherein the step of feeding a raw material gas into an inlet vessel, the step of generating a raw material gas plasma, and the step of producing a precursor comprise the step of bubbling a carrier gas through a liquid organometallic complex and vaporizing the organometallic complex, and the step of etching the perforated plate with the vaporized organometallic complex to produce a precursor composed of the metallic component contained in the perforated plate and the halogen contained in the organometallic complex.

8. An apparatus for the formation of a metal film which comprises an inlet vessel equipped with a metallic perforated plate having discharge orifices bored therethrough and adapted to receive a raw material gas in its internal volume; a first plasma generator for converting the raw material gas received in the inlet vessel into a plasma and thereby generating a raw material gas plasma; a reaction vessel housing the inlet vessel and a substrate; a rotating magnetic field generator for creating a rotating magnetic field between the perforated plate and the substrate; and a second plasma generator for generating a plasma from a reducing gas fed into the reaction vessel.

9. An apparatus for the formation of a metal film which comprises an inlet vessel equipped with a metallic perforated plate having discharge orifices bored therethrough and adapted to receive a raw material gas in its internal volume; a first

plasma generator for converting the raw material gas received in the inlet vessel into a plasma and thereby generating a raw material gas plasma; a reaction vessel housing the inlet vessel and a substrate; and an electrode for generating a plasma from a reducing gas fed into the reaction vessel by applying high-frequency electric power thereto.

10. An apparatus for the formation of a metal film which comprises an inlet vessel equipped with a metallic perforated plate having discharge orifices bored therethrough and adapted to receive a raw material gas in its internal volume; a plasma generator for converting the raw material gas received in the inlet vessel into a plasma and thereby generating a raw material gas plasma; a reaction vessel housing the inlet vessel and a substrate; and a reducing gas heating device for heating a reducing gas fed into the reaction vessel.

11. An apparatus for the formation of a metal film which comprises a precursor feeding device for bringing a raw material gas into contact with a hot metallic filament to produce a precursor and feeding the precursor into a reaction vessel; the reaction vessel housing a substrate; and a reducing gas heating device for heating a reducing gas fed into the reaction vessel.

12. An apparatus for the formation of a metal film which comprises a precursor feeding device for bubbling a carrier gas through a liquid organometallic complex, vaporizing the organometallic complex, producing a precursor from the

vaporized organometallic complex, and feeding the precursor into a reaction vessel; the reaction vessel housing a substrate; a rotating magnetic field generator for creating a rotating magnetic field in a space above the substrate; and a second plasma generator for generating a plasma from a reducing gas fed into the reaction vessel.

13. An apparatus for the formation of a metal film which comprises a precursor feeding device for bubbling a carrier gas through a liquid organometallic complex, vaporizing the organometallic complex, producing a precursor from the vaporized organometallic complex, and feeding the precursor into a reaction vessel; the reaction vessel housing a substrate; and an electrode for generating a plasma from a reducing gas fed into the reaction vessel by applying high-frequency electric power thereto.

14. An apparatus for the formation of a metal film, the apparatus comprising:

an inlet vessel equipped with a metallic discharge plate having a multitude of discharge orifices bored therethrough and adapted to receive a chlorine-containing raw material gas in its internal volume;

a chamber housing the inlet vessel and a substrate;

first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor

composed of the metallic component contained in the discharge plate and the chlorine contained in the raw material gas;

second plasma generating means for converting a hydrogen-containing reducing gas within the chamber into a plasma to generate a reducing gas plasma; and

chamber heating means for heating the chamber to a predetermined temperature;

whereby the precursor is passed through the reducing gas plasma within the chamber to remove chlorine from the precursor by reduction, without allowing the precursor to deposit on the heated inner wall of the chamber, and the resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

15. An apparatus for the formation of a metal film, the apparatus comprising:

an inlet vessel equipped with a metallic discharge plate having a multitude of discharge orifices bored therethrough and adapted to receive a chlorine-containing raw material gas in its internal volume;

discharge plate heating means for heating the discharge plate to a predetermined temperature;

a chamber housing the inlet vessel and a substrate;

first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor

composed of the metallic component contained in the discharge plate and the chlorine contained in the raw material gas; and

second plasma generating means for converting a hydrogen-containing reducing gas within the chamber into a plasma to generate a reducing gas plasma;

whereby the precursor, which has been produced by etching the heated discharge plate and is hence easy to reduce, is passed through the reducing gas plasma to remove chlorine from the precursor by reduction, and the resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

16. An apparatus for the formation of a metal film, the apparatus comprising:

an inlet vessel equipped with a metallic discharge plate having a multitude of discharge orifices bored therethrough and adapted to receive a chlorine-containing raw material gas in its internal volume;

discharge plate heating means for heating the discharge plate to a predetermined temperature;

a chamber housing the inlet vessel and a substrate;

first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor composed of the metallic component contained in the discharge plate and the chlorine contained in the raw material gas;

second plasma generating means for converting a hydrogen-containing reducing gas within the chamber into a plasma to generate a reducing gas plasma; and

5 chamber heating means for heating the chamber to a predetermined temperature;

whereby the precursor, which has been produced by etching the heated discharge plate and is hence easy to reduce, is passed through the reducing gas plasma to remove chlorine from the precursor by reduction, without allowing the precursor to
10 deposit on the heated inner wall of the chamber, and the resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

17. An apparatus for the formation of a metal film, the apparatus comprising:

15 an inlet vessel equipped with a metallic discharge plate having a multitude of discharge orifices bored therethrough and adapted to receive a chlorine-containing raw material gas in its internal volume;

a chamber housing the inlet vessel and a substrate;

20 first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor composed of the metallic component contained in the discharge
25 plate and the chlorine contained in the raw material gas;

reducing gas heating means for heating a hydrogen-

containing reducing gas to a high temperature and thereby producing an atomic reducing gas within the chamber between the substrate and the discharge plate; and

5 chamber heating means for heating the chamber to a predetermined temperature;

whereby the precursor is passed through the atomic reducing gas within the chamber to remove chlorine from the precursor by reduction, without allowing the precursor to deposit on the heated inner wall of the chamber, and the
10 resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

18. An apparatus for the formation of a metal film, the apparatus comprising:

an inlet vessel equipped with a metallic discharge plate
15 having a multitude of discharge orifices bored therethrough and adapted to receive a chlorine-containing raw material gas in its internal volume;

discharge plate heating means for heating the discharge plate to a predetermined temperature;

20 a chamber housing the inlet vessel and a substrate;

first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor
25 composed of the metallic component contained in the discharge plate and the chlorine contained in the raw material gas; and

reducing gas heating means for heating a hydrogen-containing reducing gas to a high temperature and thereby producing an atomic reducing gas within the chamber between the substrate and the discharge plate;

5 whereby the precursor, which has been produced by etching the heated discharge plate and is hence easy to reduce, is passed through the atomic reducing gas to remove chlorine from the precursor by reduction, and the resulting metallic ion is directed onto the substrate to form a metal film on the
10 substrate.

19. An apparatus for the formation of a metal film, the apparatus comprising:

an inlet vessel equipped with a metallic discharge plate having a multitude of discharge orifices bored therethrough
15 and adapted to receive a chlorine-containing raw material gas in its internal volume;

discharge plate heating means for heating the discharge plate to a predetermined temperature;

a chamber housing the inlet vessel and a substrate;

20 first plasma generating means for converting the raw material gas within the inlet vessel into a plasma to generate a raw material gas plasma, and thereby etching the discharge plate with the raw material gas plasma to produce a precursor composed of the metallic component contained in the discharge
25 plate and the chlorine contained in the raw material gas;

reducing gas heating means for heating a hydrogen-

containing reducing gas to a high temperature and thereby producing an atomic reducing gas within the chamber between the substrate and the discharge plate; and

5 chamber heating means for heating the chamber to a predetermined temperature;

whereby the precursor, which has been produced by etching the heated discharge plate and is hence easy to reduce, is passed through the atomic reducing gas within the chamber to remove chlorine from the precursor by reduction, without
10 allowing the precursor to deposit on the heated inner wall of the chamber, and the resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

20. An apparatus for the formation of a metal film, the apparatus comprising:

15 precursor feeding means for bringing a chlorine-containing raw material gas into contact with a hot metallic filament to produce a precursor within a chamber housing a substrate, the precursor being composed of the metallic component contained in the metallic filament and the chlorine
20 contained in the raw material gas;

reducing gas heating means for heating a hydrogen-containing reducing gas to a high temperature and thereby producing an atomic reducing gas within the chamber between the substrate and the discharge plate; and

25 chamber heating means for heating the chamber to a predetermined temperature;

whereby the precursor is passed through the atomic reducing gas within the chamber to remove chlorine from the precursor by reduction, without allowing the precursor to deposit on the heated inner wall of the chamber, and the resulting metallic ion is directed onto the substrate to form a metal film on the substrate.

21. An apparatus for the formation of a metal film as claimed in any one of claims 14 to 20 wherein the discharge plate or metallic filament is made of copper, so that Cu_xCl_y is produced as the precursor.

22. An apparatus for the formation of a metal film as claimed in any one of claims 15, 16, 18 and 19 wherein the discharge plate is made of copper and the predetermined temperature to which the discharge plate is heated by the discharge plate heating means is in the range of 200 to 800°C.

23. An apparatus for the formation of a metal film as claimed in any one of claims 15, 16, 18, 19 and 22 wherein the discharge plate heating means comprises means for heating the discharge plate by introducing a rare gas into the inlet vessel, using the first plasma generating means to generate a rare gas plasma, and applying a voltage so as to cause the rare gas component ion to collide with the discharge plate.

24. A method for the formation of a metal film which comprises reacting chlorine with a metallic plate within a chamber to produce a precursor composed of a metallic component and chlorine, removing chlorine from the precursor

by reduction, and directing the resulting metallic ion onto a substrate within the chamber to form a metal film on the substrate, the method being characterized in that the chamber is heated to a predetermined temperature so as to prevent the precursor from depositing on the inner wall of the chamber.

25. A method for the formation of a metal film which comprises reacting chlorine with a metallic plate within a chamber to produce a precursor composed of a metallic component and chlorine, removing chlorine from the precursor by reduction, and directing the resulting metallic ion onto a substrate within the chamber to form a metal film on the substrate, the method being characterized in that the metallic plate is heated to a predetermined temperature so as to make the precursor easy to reduce.

26. A method for the formation of a metal film which comprises reacting chlorine with a metallic plate within a chamber to produce a precursor composed of a metallic component and chlorine, removing chlorine from the precursor by reduction, and directing the resulting metallic ion onto a substrate within the chamber to form a metal film on the substrate, the method being characterized in that the chamber is heated to a predetermined temperature so as to prevent the precursor from depositing on the inner wall of the chamber and, moreover, the metallic plate is heated to a predetermined temperature so as to make the precursor easy to reduce.

27. A method for the formation of a metal film as

claimed in any one of claims 24 to 26 wherein the metal plate is made of copper, so that Cu_xCl_y is produced as the precursor.

28. A method for the formation of a metal film as claimed in claim 27 wherein the predetermined temperature to which the metallic plate is heated is in the range of 200 to 800°C.

29. An apparatus for the formation of a metal film, the apparatus comprising:

a reaction vessel in which a substrate to be treated is placed;

an inlet vessel disposed within said reaction vessel and equipped with a copper discharge plate having a plurality of discharge orifices bored therethrough;

temperature control means attached to said copper discharge plate;

a raw material gas feed pipe inserted into said inlet vessel for feeding chlorine or hydrogen chloride;

plasma generating means for generating a plasma of chlorine or hydrogen chloride within said inlet vessel;

atomic reducing gas producing means for producing an atomic reducing gas within said reaction vessel, at least in the neighborhood of said substrate to be treated; and

evacuation means for evacuating any gas from said reaction vessel and said inlet vessel.

30. An apparatus for the vapor phase growth of a thin copper film as claimed in claim 29 wherein said temperature

control means comprises a circulation pipe built in said copper discharge plate for passing a heating medium or cooling medium therethrough.

31. An apparatus for the formation of a metal film as
5 claimed in claim 29 wherein said atomic reducing gas producing means comprises a reducing gas feed pipe for feeding a reducing gas into said reaction vessel, and a plasma generator for converting the reducing gas into a plasma and thereby
10 producing an atomic reducing gas at least in the neighborhood of said substrate to be treated.

32. An apparatus for the formation of a metal film as
claimed in claim 29 wherein said atomic reducing gas producing means comprises a reducing gas feed pipe for feeding a
15 reducing gas into said reaction vessel, and a heating element for heating the reducing gas and thereby producing an atomic reducing gas at least in the neighborhood of said substrate to be treated.

33. An apparatus for the formation of a metal film, the apparatus comprising:

20 a reaction vessel in which a substrate to be treated is placed;

a raw material gas feed pipe inserted into said inlet vessel for feeding chlorine or hydrogen chloride;

25 a spiral tube attached to the inner end of said raw material gas feed pipe, having a raw material gas flow passage whose inner surface is made of copper, and equipped with a

heating element;

atomic reducing gas producing means for producing an atomic reducing gas within said reaction vessel, at least in the neighborhood of said substrate to be treated; and

5 evacuation means for evacuating any gas from said reaction vessel and said raw material gas flow passage.

34. An apparatus for the formation of a metal film as claimed in claim 33 wherein said spiral tube equipped with a heating element has a dual tubular structure consisting of an
10 outer tube and an inner copper tube inserted into said outer tube and used as a flow passage for the raw material gas, and a heating medium is made to flow through the space between said outer tube and said inner copper tube.

35. An apparatus for the formation of a metal film as
15 claimed in claim 33 wherein said spiral tube equipped with a heating element has a structure consisting of a copper tube and a tubular heater disposed around said copper tube with a tubular insulator interposed therebetween.